

# DEVELOPING AN EFFICIENT METHOD FOR THE MEASUREMENT OF ISOTOPIC URANIUM AND THORIUM IN SMALL SAMPLES OF SOILS AND ENVIRONMENTAL WATERS

**Renpo Wu, James R. Noyce and Lih-Ching Chu**

Division of Radiochemistry, Office of Environmental Safety  
Illinois Department of Nuclear Safety, Springfield

## Abstract

This paper describes an ongoing project to develop an efficient radiochemical method for sequential analyses of uranium and thorium isotopes in small samples of soils and environmental waters. Soils are first solubilized by fusing with lithium metaborate and dissolving the melt in dilute nitric acid. After reduction of any plutonium to the +3 oxidation state, uranium and thorium are extracted from the aqueous sample by bis(2-ethylhexyl)phosphoric acid (HDEHP) in toluene. They are back-extracted into 5M sulfuric acid. After decomposing residual organic material, uranium is oxidized to +6 with sodium nitrite. Thorium is microcoprecipitated with neodymium fluoride and filtered. Uranium in the filtrate is reduced with titanium (III) chloride, then microcoprecipitated and filtered in the same manner. After washing and drying the filters, they are counted by silicon-detector alpha-particle spectrometry. For spikes of deionized water, uranium and thorium recoveries are 80% or better, uranium and thorium separation is nearly quantitative, and the resolution of thorium spectra is sufficient to allow the use of  $^{229}\text{Th}$  as a tracer. Uranium is traced with purified  $^{232}\text{U}$ . The oral presentation will include results obtained after the submission of the extended abstract below.

## Extended Abstract

### *Need*

The Illinois Department of Nuclear Safety (IDNS) has the responsibility and authority for regulating all forms and users of ionizing radiation in the State, except for a few Federal facilities. The Office of Environmental Safety within IDNS is concerned with monitoring radiation and radioactivity in the environment and applying the information gained to radiological protection. Several sites in Illinois either contain or hold the potential for having elevated levels of alpha-particle-emitting nuclides, particularly uranium and thorium. The Division of Radiochemistry performs isotopic measurements of uranium and thorium by radiochemical separations followed by alpha-particle spectrometry, or by gamma-ray spectrometry of their decay progeny.

Our radiochemical analyses have been very sensitive but slow, while our gamma-ray analyses are less sensitive but faster. A need exists for a quicker radiochemical method that retains the sensitivity and specificity of our existing procedure. The present sequential actinide separation procedure requires after sample preparation, for uranium and thorium alone, an initial coprecipitation, an anion exchange column, a second anion exchange column for uranium, and separate solvent extractions. After its back extraction, each radioelement is electrodeposited, from chemically different solutions, for silicon-detector alpha-particle spectrometry.

## ***Goals***

We are striving for a method with these characteristics:

- Is a simple but reliable analysis for uranium and thorium
- Provides isotopic information
- Is suitable for environmental waters, soils and fresh-water sediments
- Measures the recoveries of uranium and thorium for each sample
- Has a small number of separation steps
- Avoids use of perchloric acid or fuming nitric acid
- Generates small volumes of wastes
- Requires no more than two work days to process eight samples from the start of sample preparation to the initiation of alpha-particle spectrometry
- Removes more than 99.5% of other radioelements that would interfere spectrally ( $^{239}\text{Pu}$ ,  $^{241}\text{Am}$ , and especially the naturally occurring  $^{226}\text{Ra}$  and  $^{210}\text{Po}$ )
- Recovers uranium and thorium 80% or better for waters, and 70% or better for soils
- Produces thorium spectra with enough resolution to allow routine use of  $^{229}\text{Th}$  as a tracer.

## ***Approaches and Problems***

The goal when beginning this work was produce a simple screening method for uranium and thorium separated from the sample matrix and other radioelements, but not from each other. The intended analysis method was a separation by an extractive scintillator and measurement by photon-electron-rejecting alpha liquid scintillation (PERALS<sup>®</sup>). We tried Thorex<sup>®</sup> (which can also extract uranium), but under our conditions a stable emulsion formed between the aqueous and organic phases. We then found that a single extraction with Alphaex<sup>®</sup> worked well, once we had determined the optimum pH for this extraction. The combined uranium-thorium spectrum has three peaks. If one assumes that both the  $^{238}\text{U}$  and  $^{232}\text{Th}$  decay series are in secular equilibrium, then the radioactivity concentrations of  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{230}\text{Th}$ ,  $^{232}\text{Th}$  and  $^{228}\text{Th}$  can be calculated by a pair of simultaneous equations and defining each concentration in terms of these two equations. The only interference usually encountered is  $^{235}\text{U}$ , but by assuming that the uranium in the sample is of normal isotopic composition,  $^{235}\text{U}$  can be corrected for.

This method was tested successfully for these five radionuclides using Rocky Flat Soil SRM<sup>®</sup> 4353, with no more than a ten percent bias. Radium, plutonium and americium were removed well. However, at this point our overall goal changed somewhat. We decided that we wanted to separate uranium and thorium and use silicon-detector alpha-particle spectrometry because (a) we had only one PERALS<sup>®</sup> instrument but 12 silicon detectors and (b) tracers could be used for uranium and for thorium recoveries. This approach also has the advantage of being able to give correct results when either or both of the uranium and thorium decay series is out of secular equilibrium. Because we did not need the scintillator in Alphaex<sup>®</sup> for silicon-detector spectrometry, we demonstrated that we could extract uranium and thorium into 0.5M HDEHP in toluene as well. The latter reagent is less expensive.

We tried several approaches for removing uranium and thorium from Alphaex<sup>®</sup> (or HDEHP reagent). Direct evaporation of the extractant or its attempted destruction by strong acids and 30% hydrogen peroxide left residue that interfered with the resolution of peaks in the alpha-particle spectra. Back extraction into 0.5M ammonium carbonate worked satisfactorily, but

required subsequent decomposition of that reagent, with sometimes reduced recovery of thorium. Most recently we tried 5M sulfuric acid as the back extractant. This appears to work well and has the advantage of not needing to convert or decompose the extractant after use.

Separation methods for uranium and thorium tried include an anion exchange column using 1-X8 resin, a U/Teva<sup>®</sup> chromatographic resin column, and microcoprecipitation with cerium fluoride or with neodymium fluoride with manipulation of uranium oxidation states (for example, see Sill (1987)). The column methods could produce satisfactory separations. However, they were not as rapid as we wanted as they required a relatively large sample volume and/or low flow rate. Changing the oxidation state of uranium to separate it from thorium has the considerable advantage of easily being made a part of the microcoprecipitation process, which reduces the total number of steps in the method.

Some of the methods leading up to the present method were tested with actual soil and water samples. Up to now, we regularly experienced several problems with the results obtained, even with spiked deionized water. Uranium recoveries were occasionally low, for no readily apparent reason. Thorium recoveries were more variable and with a lower average than for uranium. Even more serious were the often incomplete removals of uranium from the thorium fraction, and the occasional incomplete removal of uranium from the thorium fraction.

### ***Present Method and Results***

The present version of the method is summarized in the Abstract. Details of the method, for water and for soil, are given in the accompanying flow chart. Silicon-detector alpha-particle spectrometry results to date are given below. Of all our results to date, these come the closest to meeting our goals. (The samples were made from one of the test waters that we used when we participated in a round-robin to qualify the PERALS<sup>®</sup> method for total uranium analyses of drinking waters, as reported by Duffey et al. (1997). This test water also contains <sup>226</sup>Ra as a contaminant.) More tests of the current version using spiked deionized water are in progress.

<u>Sample ID</u>	Recovery, %		Purity		Maximum FWHM, keV	
	<u>Of U</u>	<u>Of Th</u>	<u>Of U</u>	<u>Of Th</u>	<u>Of U</u>	<u>Of Th</u>
ASTM(9)2-7	82	93	high	high	76	56
ASTM(9)2-8	89	86	high	high	103	81

### ***Conclusions***

We have learned that specific conditions in several steps are essential to achieve good quality results. Listed in the order that they are encountered in the method, these conditions are:

1. Use only radioisotopically pure <sup>229</sup>Th tracer, so as to not add other thorium isotopes to samples. We have found NIST SRM<sup>®</sup> 4328A to be suitable. (Short-lived decay products of <sup>229</sup>Th and from <sup>228</sup>Th in the sample soon appear in the thorium fraction spectrum, but do not interfere because all their energies sufficiently exceed that of <sup>228</sup>Th).
2. Use only radioisotopically pure <sup>232</sup>U tracer, so as not to add other uranium isotopes to samples. In addition, due to its relatively short half-life (69.8 y), the <sup>232</sup>U tracer solution must be periodically purified from its progeny, especially <sup>228</sup>Th. (We have used the

method of Sill (1974) for this purpose. After the initial preparation of the “self-cleaning” tracer, the solution is standardized by adding a known quantity of a certified reference material solution of another uranium isotope as a tracer, and measuring by silicon-detector alpha-particle spectrometry.)

3. Adjustment of the sample's pH to 0.72 to 0.74 is essential to obtain total extraction of uranium and thorium into the HDEHP/toluene reagent concurrent with minimal extraction of trivalent actinides.
4. Complete reduction of plutonium to the +3 oxidation state is necessary to preclude its extracting into the HDEHP/toluene reagent.
5. Five molar is the optimum sulfuric acid concentration for thorough removal of thorium and uranium from the organic phase without adding excessive acid that must then be fumed off the sample in the next step (Dacheux and Aupiais (1997), fig. 3).
6. Use freshly prepared sodium nitrite solution to assure the oxidation of all uranium before coprecipitating thorium on neodymium fluoride.
7. Use titanium (III) chloride of full potency to be sure that all uranium is reduced prior to coprecipitating it with neodymium fluoride.
8. Heat the filter to dryness at a temperature sufficient to expel any acid residue and radon, but not so high as to make the filter curl.

### ***Future Efforts***

We think that the present method is nearly ready to be tested with actual samples. We will analyze environmental waters, unspiked and spiked with uranium and thorium, with yield tracers. We will analyze Rocky Flats Soil SRM<sup>®</sup> 4353, with yield tracers. We want to extend the use of this method to fresh-water sediments, so we hope to locate and use a certified reference material of fresh-water sediment with certifications for the appropriate isotopes of uranium and thorium. Other possible future work could be to try expanding the method to analyze additional actinides and/or radium from the same sample as uranium and thorium are.

### ***References***

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